H. H. DOW, W. S. GATES & A. E. SCHAEFER.

METHOD OF ELECTROLYZING NICKEL SULFATE SOLUTIONS.

APPLICATION FILED APR. 11, 1907.

1,003,092. **Patented Sept. 12, 1911.**

2 SHEETS—SHEET 1.

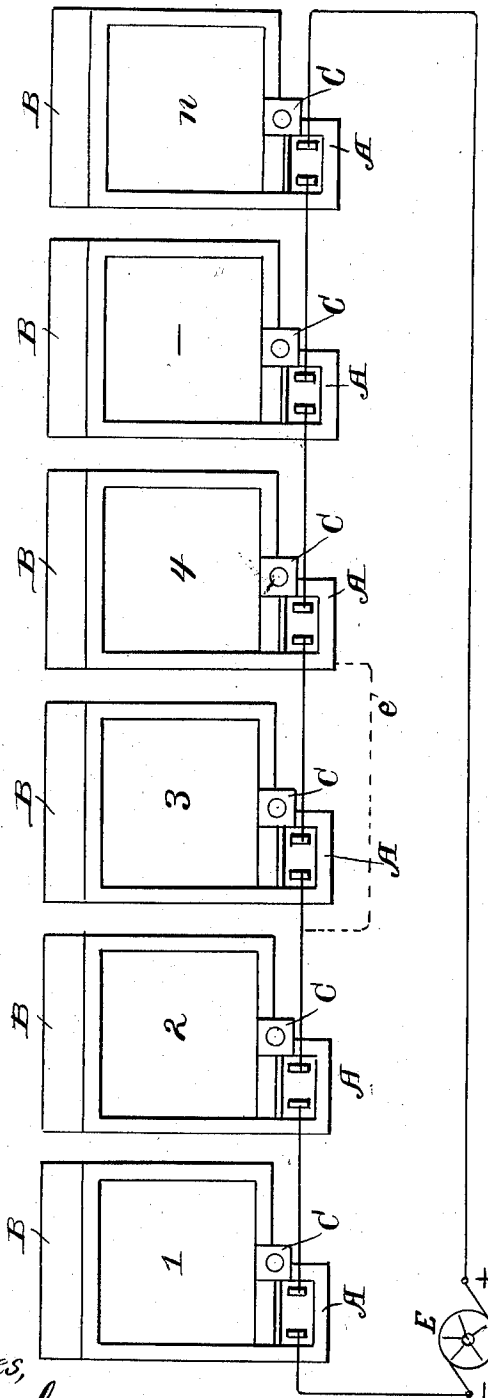

Fig. 1.

Witnesses,
M. Israel
Jno. F. Oberlin

Inventors,
Herbert H. Dow,
Walter S. Gates and Arthur E. Schaefer
By J. B. Fay
their attorney

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2 SHEETS—SHEET 2.

Fig. 2

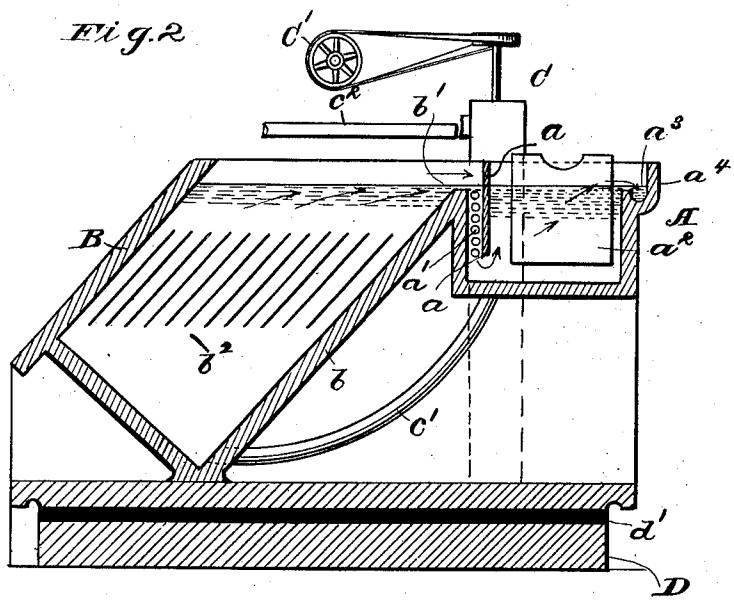
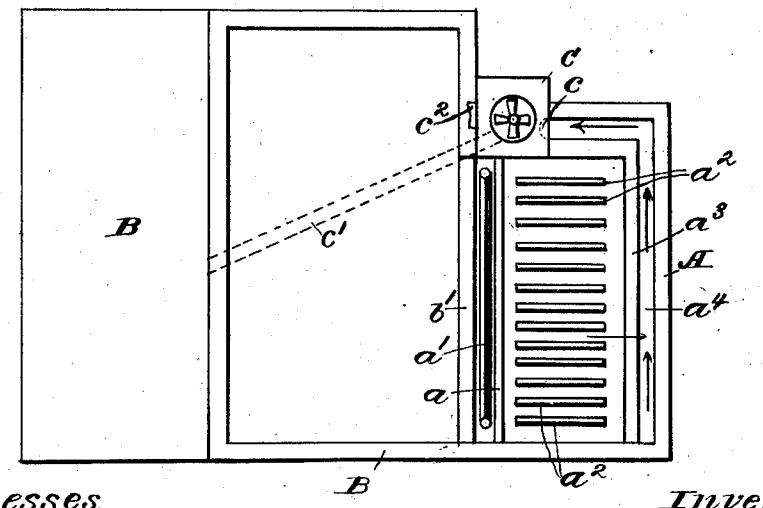


Fig. 3



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their attorney

UNITED STATES PATENT OFFICE.

HERBERT H. DOW, OF MIDLAND, MICHIGAN, AND WALTER S. GATES AND ARTHUR E. SCHAEFER, OF WORTHINGTON, ONTARIO, CANADA, ASSIGNORS TO THE ONTARIO NICKEL COMPANY, LIMITED, OF WORTHINGTON, CANADA, A CORPORATION.

METHOD OF ELECTROLYZING NICKEL-SULFATE SOLUTIONS.

1,003,092. Specification of Letters Patent. **Patented Sept. 12, 1911.**

Application filed April 11, 1907. Serial No. 367,696.

To all whom it may concern:

Be it known that we, HERBERT H. DOW, residing at Midland, county of Midland, Michigan, and WALTER S. GATES and ARTHUR E. SCHAEFER, residing at Worthington, district of Algoma, Ontario, Canada, citizens of the United States, have invented a new and useful Improvement in Methods of Electrolyzing Nickel-Sulfate Solutions, of which the following is a specification, the principle of the invention being herein explained and the best mode in which we have contemplated applying that principle, so as to distinguish it from other inventions.

This invention relates, in general, to the art of recovering metallic nickel from basic nickel precipitates, and more specifically to an improved method for the electrolysis of the nickel sulfate into which basic nickel precipitates are converted preliminarily to such electrolysis in one approved course of procedure for effecting such recovery. Now in electrolyzing nickel sulfate in the presence of water with insoluble anodes, there is formed at the anode an amount of sulfuric acid proportional to the amount of nickel deposited on the cathode, in accordance with the well-known reaction:

$$NiSO_4+H_2O=Ni+H_2SO_4+O.$$

As the electrolysis proceeds, the electrolyte becomes more and more acid, resulting in a lowering of the ampere efficiency until it finally reaches or approximates zero, and the passing of the current no longer results in the deposition of nickel. This gradual diminution in the ampere efficiency is due to the fact that, with the creation of sulfuric acid in the solution a secondary electrolysis takes place, the sulfuric acid, or rather the water acidulated with sulfuric acid, being decomposed as follows:

$$H_2SO_4+H_2O=H_2+H_2SO_4+O$$

and H_2 is deposited at the cathode in place of nickel. Since the voltage of decomposition of sulfuric acid in aqueous solution is less than that of nickel sulfate in aqueous solution, this secondary reaction takes place in preference to the decomposition of nickel sulfate, and as the amount of free acid increases, the amount of nickel deposited decreases proportionately. A further cause for the aforesaid diminution in ampere efficiency is based on the fact that the sulfuric acid created in the solution exercises a solvent effect on the nickel already deposited. While this solvent action is negligible if the amount of acid be small, it becomes more pronounced as the percentage of acid increases until finally the amount of nickel dissolved at the cathode equals the amount deposited and a state of equilibrium is thus reached. It is therefore evident that, in order to produce metallic nickel on a commercial scale by the electrolysis of nickel sulfate solutions, it is imperative to maintain the electrolyte, at or nearly at, a state of neutrality. It is also evident that some nickel-containing substance should be used for destroying this acidity in order that the electrolyte should not become impoverished in nickel. In other words, the ideal condition for a continuous process would be that in which there is continuously as much nickel dissolved from the nickel-containing substance and added to the electrolyte as there is nickel taken from the electrolyte and deposited on the cathode. As the presence of free acid in the electrolyte must be kept low, it is evident that a nickel-containing substance must be used which is readily dissolved by a very dilute sulfuric acid solution. It is also of great advantage that this substance should not contain a serious amount of impurities of such a kind that they will become soluble in the electrolyte along with the nickel, or will be suspended therein and later have to be removed by some additional reagent, or else be allowed to become deposited with the nickel, thereby injuring the quality of the latter. Some of the common forms of nickel, which might be used for this purpose were they suitable, are the metal, as plates, bars and shot; oxid; matte; and insoluble precipitated compounds. Objections, however, are to be found to the use of most of these. Thus freshly electro-deposited nickel is quite readily attacked by dilute sulfuric acid (thereby lowering the ampere efficiency of the cell), but in the form of bars and plates is too slowly attacked to serve as a means for neutralizing the electrolyte in refining on a commercial scale. Moreover, crude metallic nickel, as ordinarily obtainable, contains considerable impurities as iron, carbon, silicon, sulfur, copper, etc., which

would contaminate the bath and deposit with the nickel. Thus the ordinary nickel anodes, such as are used in electro-plating, contain iron in such quantity as to require special steps to be taken looking toward its removal, usually involving the addition of ammonia to the bath. Nickel oxid is not rapidly attacked by dilute sulfuric acid; while matte contains a relatively large proportion of foreign matter, chiefly sulfur, copper, and iron, which render it unsuitable for use in this connection. The substance best adapted to this purpose has been found to be nickel in the form of basic nickel precipitate as for instance nickel hydrate, this partly being due to its more readily disseminative character and the ease with which it is manipulated. However, its satisfactory employment by methods heretofore prevailing in the electrolytic recovery of nickel has not been possible without either encountering considerable expense in first purifying it of the precipitates of other metals which are always involved therewith, or else acquiescing in the deposition of an impure product.

The object then of our present invention is to provide a method of thus neutralizing the electrolyte in which, to a very large degree, the objectionable features above enumerated have been eliminated.

To the accomplishment of this and related ends such invention, then, consists of the steps, and the means for carrying out the same, hereinafter fully described and specifically set forth in the claims.

The annexed drawings and the following description set forth in detail certain means embodying the invention, and one mode of carrying out the same, such disclosed means and mode, however, constituting but one of various ways in which the principle of the invention may be used.

In said annexed drawings: Figure 1 is a plan view of a proposed system for the electro-deposition of nickel from a solution of nickel sulfate, in accordance with our improved method; Fig. 2 is a vertical transverse cross-section of one of the units of such system; and Fig. 3 is a plan view, on a larger scale than in Fig. 1, of one of such units.

The illustrative apparatus thus shown for carrying out our improved process may properly be briefly described before entering upon the details of such process.

From an inspection of the foregoing figures it will be noted that each of the units above referred to comprise the combination of an electrolytic cell A, separating means in the form of a settling tank B, and agitating or mixing means in the form of a helicoidal mixing pump C. Such cell, settling tank and agitator are preferably built up in the form of a substantially integral structure, mounted on a common base D, from which they are thoroughly insulated by means of a thick interposed layer of insulating material d'. The settling chamber B may be of any of the accepted types of construction, but we use by preference the hopper-shaped louver type illustrated, which we have found in actual experience to be well suited to our purpose. In this style of settler, the mixture is distributed by means of the distributing trough hereinafter to be described, between or over the various inclined glass plates b^2 constituting the main feature of this form of settling device. The mixture from the agitator is thereby separated into a heavy mixture of liquid and precipitate, or sludge, which falls to the bottom of the hopper, and a clear purified solution which rises to the top of the settler.

The electrolytic cell A, which is of oblong rectangular form, is preferably disposed closely adjacent to the outwardly inclined side or wall b of the hopper-shaped settling-tank B, and such outwardly inclined side is made lower than the other walls of the tank so as to form an overflow from the tank into the cell, the upper edge of the side forming a weir b'. A baffle or deflecting plate a is disposed directly in front of such overflow and weir, being removed only a small distance from the proximate cell wall. By means of such plate, it will be evident that the current overflowing from the tank will be deflected downwardly and enter the cell A, proper, from below. In the space intermediate of such baffle plate and adjacent cell wall are disposed heater coils a' of lead, whereby such deflected current may be heated if desirable or necessary. Suitably supported within the cell are disposed a series of electrodes a^2 of familiar construction, and hence not requiring detailed description here. The wall of the cell opposite to the tank overflow is likewise provided with a weir a^3, forming an overflow, and with a gutter a^4 adapted to receive the liquid escaping thereover, and conduct the same to the aforesaid mixing pump C. The pump chamber of this pump C is preferably located in the angle formed by the end of the cell, A, with the settling tank B, and is adapted to receive the liquid overflowing from the cell in the manner just described, through a suitable aperture c opening into the upper portion of such chamber. The lower portion of the pump chamber is connected by means of a conduit c' with the lower portion of the settling tank, and the helicoidal mixing mechanism of the pump is designed, when properly operated, to exert a suction effect through this conduit whereby the contents of the lower portion of the settler tank will obviously be drawn to the pump. The sludge which composes

such lower layer of the contents of the tank, is thus raised and mixed with the liquid overflowing from cell A and the resultant mixture is discharged through a discharge pipe or trough c^2 therefor provided. By means of this trough, the mixture from the pump can be conveniently diverted to the several sections of the upper portion of the settling tank, as may be desired. Suitable means for effecting the operation of the mixing pump are of course provided, such as a power-driven counter-shaft C′ with belt and pulley. A battery of such settling tanks and cells, with connecting mechanism, including the mixture pump described, constitutes a system such as is shown in Fig. 1. As will there be seen, the current from the dynamo E is passed in series through the several electrolytic cells B of the successive units of the system. When it is desired to cut out any one of the units of the set, as for repairs, cleaning, or the like, this is readily accomplished by bridging around the same with a movable conductor *e* without interrupting the operation of the system as a whole.

To continue, then, the discussion of our method, having regard for the sake of concrete illustration to the form of apparatus just described for the carrying out of the same, we utilize basic nickel precipitate to neutralize the free acid produced by the electrolysis of the sulfate solution as has been previously stated. We do not, however, add such precipitate to the electrolyte in the cell but do this apart from the latter. Assuming, then, the apparatus to be in operation, the settling tank B will be charged with a mixture of the sulfate solution and a sufficient excess of basic precipitate to more than insure the neutrality of the former. Such mixture, by virtue of the action of the louver plates of the settler, is separated into a relatively heavy mixture, or sludge, which gradually falls to the bottom of the tank and a clear, or relatively clear, neutral and purified nickel solution, which rises to the top of the settler. The sludge or heavy mixture, consisting chiefly of the excess of basic nickel precipitate, is withdrawn by the action of the mixing pump through tube c' and subsequently treated as will appear. The clear and neutralized nickel sulfate solution overflows from the top of the settling chamber of weir into electrolytic cell A, being heated when desired by means of the heating coil a'. The deflecting plate *a*, in addition to directing the current, thus overflowing into the cell, across the heating coil, effects the discharge thereof at or near the bottom of the electrodes a^2, in such a manner as to secure a good circulation of the fresh electrolyte throughout the cell. As the electrolyte rises and becomes acid, owing to the deposition of the nickel therefrom and the consequent liberation of the acid radical of the sulfate, it overflows at the top into the gutter a^4, and is thence conducted into the mixing chamber C where it meets the rising mixture of sludge drawn by the action of the pump from the bottom of the settling chamber. Here the complete neutralization of such acid electrolyte is obviously promptly effected, according to the well known reactions

$$NiO_2H_2+H_2SO_4=NiSO_4+2H_2O.$$
$$NiO_2H_2+NiCO_3+2H_2SO_4=2NiSO_4+3H_2O+CO_2.$$

The resultant mixture of neutralized electrolyte and sludge is then discharged in the upper portion of the settling tank, there to undergo the process of separation as before, and the solid and liquid ingredients thereof to go again the rounds just described. It will thus be seen that both the basic precipitate and the nickel sulfate electrolyte are continually moving in separate currents, which circuits, however, overlap and become one in the mixing chamber.

The size of the settler is determined by the minimum degree of acidity, which it is desirable to maintain in the cell, since a lower degree of acidity calls for the agitation and settling of much more precipitate and electrolyte in a given time. The settler size also depends, somewhat, on the degree of clarity of the neutralized liquor desired. With a very pure basic precipitate, fresh electrolyte may run into the cell while slightly turbid, the minute particles in the liquid tending to keep down the acidity of the cell. If, however, the number of particles in the incoming electrolyte are in excess of what will be decomposed by the acid in the solution, or if the particles are insoluble in the acid, the resulting deposit of the nickel will become warty, owing to the mechanical inclosure of these particles in the cathode deposit. The term "separating", or "settling", as herein employed to designate the operation taking place in the settling tank B, it will, hence be understood, is employed in a relative sense only. Thus, having reference to such settling tank specifically as the means for effecting this separation, such term means a subsiding of the excess of the precipitate in a mixture of liquid and precipitate whereby the precipitate becomes most dense at the lower part of the container, leaving above it a supernatant layer of clear, or nearly clear liquid containing substantially no precipitate.

As the deposition of nickel proceeds, with the consequent formation of free acid and the solution of the basic nickel precipitate by the acid thus formed, the amount of basic nickel precipitate in the system will of course gradually diminish, and may be replenished from time to time by the addition

of more precipitate. This addition may continue until the impurities in the system accumulate to such an extent that the basic compound of nickel is no longer in sufficient excess to prevent impurities entering into solution in the mixing chamber, in spite of the purifying action normally occurring there to which reference will presently be more particularly made. The system may be run either intermittently, removing all the basic precipitate with accumulated impurities at stated intervals and substituting therefor a fresh and purer precipitate; or better, the system may be run continuously by withdrawing a certain portion of the impure precipitate and replacing the same with an equivalent amount of fresh and purer precipitate without interrupting the electrolytic action. In this latter, continuous process, the impure precipitate may be purified outside of the system in any approved fashion, and the valuable residuum then returned to the system to replace other impure basic precipitate.

The conditions in the cell, such as the current density, composition of electrolyte, temperature of electrolyte, etc., are regulated to secure the best deposits from a commercial standpoint. As has been shown the neutralized electrolyte may be advantageously warmed if desired, by inserting an insulated steam coil, in the path of the electrolyte as it flows from the settler to the electrolytic cell. It should be mentioned that it is desirable that the electrolyte be free from soluble chlorids, since these are decomposed by electrolysis with the formation of free chlorin which oxidizes basic nickelous compounds to nickelic hydrate. This latter compound is insoluble in the acid electrolyte and therefore useless as far as the electrolysis is concerned.

We are aware that it has been proposed to neutralize the sulfuric acid formed in the electrolysis of nickel sulfate by the addition of nickel hydrate to the electrolyte in the cell. This method possesses the disadvantage of producing a turbid electrolyte, resulting in the production of warty and contaminated deposits. We are not aware that it has been proposed to neutralize the acid electrolyte in a separate compartment apart from or outside of the cell, or that any means have been employed in this connection for clarifying the turbid neutralized solution, much less for returning the separated nickel precipitate to neutralize another portion of acid electrolyte. We should also point out this substantial difference between our new and improved method and other methods for the disposal of the free acid formed in the electrolysis of nickel sulfate solutions, namely, that other methods effect merely the conversion of combined nickel to metallic nickel, retaining all the impurities in the original nickel-containing compound, whereas in our method we effect a purification or refining of the nickel as well as a reduction thereof to the metallic condition. For the agitation in the mixing chamber not only effects the neutralization of the electrolyte, but also serves as a purification process. Thus if the electrolyte contains any metals in solution, as Fe, Al, Cu, Mn, Zn, etc., whose basic compounds are more insoluble than the corresponding basic compound of the nickel contained in excess in the mixer, these metals will be precipitated as the corresponding basic compound and an equivalent amount of pure nickel sulfate will be formed. Similarly, if at that portion of the mixing chamber, where the acid electrolyte enters, the excess of acid should dissolve from the impure basic precipitate any of the beforementioned metals, these will again be precipitated on being agitated with the excess of the basic nickel precipitate, and a pure, or nearly pure, nickel solution will result. This method of purification of metal precipitates, apart from any combination thereof with other steps such as are disclosed in this present process, forms the subject-matter of Patent No. 956,763, issued to two of the present inventors on May 3, 1910. It is therefore obvious that in employing this method to produce an electrolytic nickel of a given purity, a much more impure basic nickel compound may be used than in methods in which the basic nickel compound is dissolved directly in the electrolytic cell, since in this latter case all the impurities contained in the said basic compound enter the electrolyte directly and are deposited along with the nickel on the cathode. It follows that a much purer electrolytic nickel may be produced by our method from a basic nickel compound of given purity than by the older method. At the same time the positive circulation of the electrolyte in the cell possesses the two-fold advantage of rapidly removing the acid electrolyte and also of bringing neutral and strong electrolyte into direct contact with the cathodes, at which places, with no circulation, the electrolyte soon becomes impoverished in nickel. Finally, this process treatment, by permitting the use of an excess of the precipitate to effect the neutralization of the acid electrolyte, in addition to maintaining the substantial purity of the latter as above explained, renders the process much more nearly automatic, since constant attention in controlling the addition of the precipitate directly to the cell where this method prevails, is entirely unnecessary.

Other modes of applying the principle of our invention may be employed instead of the one explained, change being made as regards the process herein disclosed, provided the step or steps stated by any one of the

following claims or the equivalents of such stated step or steps be employed.

We therefore particularly point out and distinctly claim as our invention:—

1. In a continuous process of recovering nickel from nickel sulfate, the recurring cycle of steps which consist in electrolyzing a solution of such sulfate, agitating the resulting acid electrolyte with basic nickel precipitate apart from the electrolytic cell for the purpose of refining and reducing the nickel, separating the mixture thus formed into its liquid and solid constituents, and then returning the separated neutral electrolyte to such cell to be further electrolyzed.

2. In a continuous process of recovering nickel from nickel sulfate, the recurring cycle of steps which consist in electrolyzing a solution of such sulfate, agitating the resulting acid electrolyte with an excess of basic nickel precipitate apart from the electrolytic cell for the purpose of refining and reducing the nickel, settling the mixture thus formed, and then returning the supernatant neutral electrolyte to such cell to be further electrolyzed.

3. In a process of recovering nickel from nickel sulfate, the steps which consist in electrolyzing a solution of such sulfate, agitating the resulting acid electrolyte with an excess of basic nickel precipitate apart from the electrolytic cell for the purpose of refining and reducing the nickel, separating the mixture thus formed into its liquid and solid constituents, returning the former of such constituents to such cell to be further electrolyzed and subsequently treating the same with the latter of such constituents.

4. In a process of recovering nickel from nickel sulfate, the steps which consist in electrolyzing a solution of such sulfate, agitating the resulting acid electrolyte with an excess of basic nickel precipitate apart from the electrolytic cell for the purpose of refining and reducing the nickel, settling the mixture thus formed, returning the supernatant neutral electrolyte to such cell to be further electrolyzed, and returning the settlings of basic nickel precipitate to neutralize the acid electrolyte thereupon again produced.

5. In a continuous process of recovering nickel from nickel sulfate, the recurring cycle of steps which consist in electrolyzing a solution of such sulfate, agitating the resulting acid electrolyte with an excess of basic nickel precipitate apart from the electrolytic cell for the purpose of refining and reducing the nickel, separating the mixture thus formed into its liquid and solid constituents, returning the former of such constituents to such cell to be further electrolyzed, and subsequently treating the same with the latter of such constituents.

6. In a continuous process of recovering nickel from nickel sulfate, the recurring cycle of steps which consist in electrolyzing a solution of such sulfate, agitating the resulting acid electrolyte with an excess of basic nickel precipitate apart from the electrolytic cell for the purpose of refining and reducing the nickel, settling the mixture thus formed, returning the supernatant neutral electrolyte to such cell to be further electrolyzed, and returning the settlings of basic nickel precipitate to neutralize the acid electrolyte thereupon again produced.

7. The process of recovering nickel from nickel sulfate, which consists in passing a solution of such sulfate and a mixture containing basic nickel precipitate successively through agitating and separating means, and electrolyzing such solution as it passes from the latter to the former, passage through the agitating means being for the purpose of both reducing and refining the nickel.

8. The process of recovering nickel from nickel sulfate, which consists in passing a solution of such sulfate and a mixture containing basic nickel precipitate successively through an agitating and a settling chamber, and electrolyzing such solution as it passes from said settling chamber to said agitating chamber, passage through the agitating chamber being for the purpose of both reducing and refining the nickel.

Signed by me, HERBERT H. DOW, at Cleveland, Ohio, this 15th day of March, 1907.

HERBERT H. DOW.

Attested by—
D. S. DAVIES,
JNO. F. OBERLIN.

Signed by me, WALTER S. GATES, at Midland, Mich., this 4th day of January, 1907.

WALTER S. GATES.

Attested by—
A. N. PATRIARCHE,
THOS. GRISWOLD, Jr.

Signed by me, ARTHUR E. SCHAEFER, at Worthington, Ontario, this 24th day of January, 1907.

ARTHUR E. SCHAEFER.

Attested by—
A. N. PATRIARCHE,
C. J. STROSACKER.